

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 09 January 2001 (09.01.01)	
International application No. PCT/EP00/04397	Applicant's or agent's file reference TS 0853 PCT
International filing date (day/month/year) 09 May 2000 (09.05.00)	Priority date (day/month/year) 13 May 1999 (13.05.99)
Applicant GOSSELINK, Johan, Willem et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
30 November 2000 (30.11.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Juan Cruz Telephone No.: (41-22) 338.83.38
-----------------------------------------------------------------------------------------------------------------------------------	---------------------------------------------------------------------

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference TS 0853 PCT	FOR FURTHER ACTION		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/EP 00/ 04397	International filing date (day/month/year) 09/05/2000	(Earliest) Priority Date (day/month/year) 13/05/1999	
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.			

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1
☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/04397

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G47/00 C10G47/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 463 611 A (HARITATOS NICHOLAS J ET AL) 26 August 1969 (1969-08-26) cited in the application the whole document ----	1-11, 18
X	US 3 224 958 A (NICHOLAS HARITATOS ET AL) 21 December 1965 (1965-12-21) cited in the application the whole document Y	1-11, 16-18
X	DE 18 16 828 A (SHELL) 31 July 1969 (1969-07-31) the whole document ----- -/-	15-17 1-11, 18

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

24 August 2000

Date of mailing of the international search report

06/09/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Michiels, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/04397

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 189 538 A (JACK POHLENZ) 15 June 1965 (1965-06-15) cited in the application the whole document ---	1-18
Y	EP 0 214 717 A (MOBIL OIL CORP) 18 March 1987 (1987-03-18) the whole document -----	15-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/04397

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3463611	A	26-08-1969	NONE	
US 3224958	A	21-12-1965	NONE	
DE 1816828	A	31-07-1969	NL 6717666 A FR 1597013 A GB 1210120 A	01-07-1969 22-06-1970 28-10-1970
US 3189538	A	15-06-1965	NONE	
EP 0214717	A	18-03-1987	AU 587032 B AU 5806986 A BR 8602872 A JP 61296089 A ZA 8604029 A	03-08-1989 24-12-1986 17-02-1987 26-12-1986 27-01-1988



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ :

C10G 47/00, 47/16

A1

(11) International Publication Number:

WO 00/69990

(43) International Publication Date: 23 November 2000 (23.11.00)

(21) International Application Number:

PCT/EP00/04397

(22) International Filing Date:

9 May 2000 (09.05.00)

(30) Priority Data:

99303733.2

13 May 1999 (13.05.99)

EP

(71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and

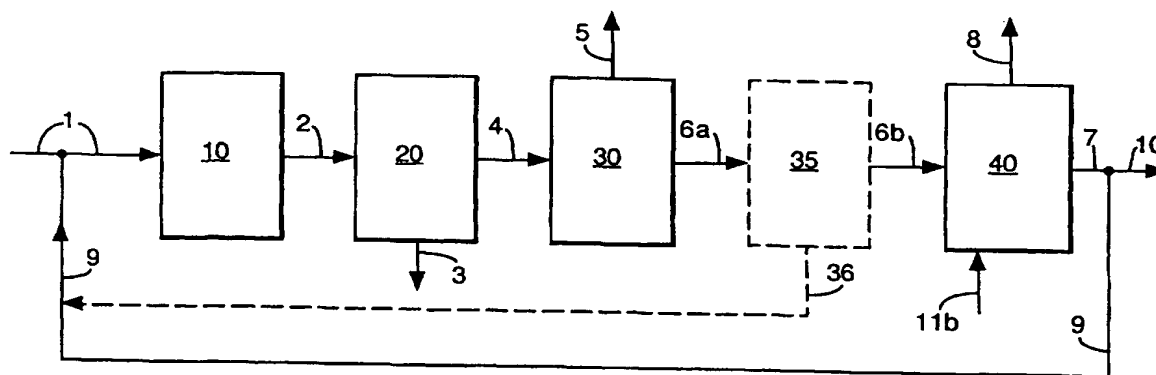
(75) Inventors/Applicants (for US only): GOSSELINK, Johan, Willem [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). GROENEVELD, Michiel, Jan [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). NOWAK, Andreas, Karl [DE/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). ROOVERS, Antonius, Adrianus, Maria [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).

(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: HYDROCARBON CONVERSION PROCESS



(57) Abstract

Method for producing hydrogen and a hydroprocessed product from a hydrocarbonaceous feedstock by subjecting it to a catalytic hydrocracking treatment using hydrogen which has been at least partly produced from hydrocracked feedstock and subjecting at least part of the hydrocracked feedstock, after having subjected it to a separation treatment in the event that hydroprocessed product is to be recovered, to a treatment to produce hydrogen in a single operation which hydrogen is at least partly recovered as product.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

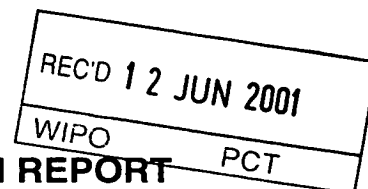
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)





Applicant's or agent's file reference TS 0853 PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/04397	International filing date (day/month/year) 09/05/2000	Priority date (day/month/year) 13/05/1999
International Patent Classification (IPC) or national classification and IPC C10G47/00		
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAP. ... et al		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.
 - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 13 sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 30/11/2000	Date of completion of this report 08.06.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Pielka, I Telephone No. +49 89 2399 8357 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/04397

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17):*)
- Description, pages:**

1-3,12,14	as originally filed		
4,4a,5-11,13	as received on	28/03/2001 with letter of	21/03/2001

Claims, No.:

1-18	as received on	28/03/2001 with letter of	21/03/2001
------	----------------	---------------------------	------------

Drawings, sheets:

1	as originally filed
---	---------------------

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/04397

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-18
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-18
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

- 2. Citations and explanations**
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

V- Reasoned statement

Novelty

1. Claim 1 relates to a process of producing a hydroprocessed product and hydrogen from a hydrocarbonaceous feedstock which comprises subjecting the feedstock to a catalytic hydrocracking treatment using hydrogen at least partly produced from the hydrocracked feedstock, the amount of hydrogen produced being in excess of that required by the process.

This subject-matter is novel over the prior art disclosed in US-A-3 224 958, or D1, and US-A-3 463 611, or D2, both having been cited in the Search report as well as in the application itself.

D1 discloses a process where feedstock is catalytically hydrocracked, the effluent passing to a separation zone where hydrocarbon product is separated and a gas rich in hydrogen is separated, passing to a partial combustion zone to produce substantially pure hydrogen which passes to the reaction zone (see claims 1, 2, 4, 7). However, there is no hydrogen product, all the hydrogen being consumed in the process.

In D2 hydrocarbon feedstock is hydrocracked, the effluent passing to a separator to produce a recycle gas, from which a purge gas is removed and partially oxidized to form hydrogen which is then separated and passed back to the hydrocracking zone (see claims 1, 4, 5 and 6). The process is not a net hydrogen producing process.

Claim 1 meets the requirements of **Article 33(2) PCT**.

Inventive Step

1. D1 and D2 are directed to recovering hydrocarbons (D1) or sulphur (D2) whilst the application is directed to recovering hydrogen and hydrocarbons. In the application the hydrocracking step is operated such that a large amount of lower boiling materials are produced, which in turn leads to an increase in the amount of hydrogen. In the prior art the production of low boiling materials is not suggested

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/04397

and the hydrocracking process is a net hydrogen consuming process. Thus the claimed subject-matter is not derivable from either D1 or D2 and involves an inventive step.

Certain Observations

1. The subject-matter of claims 11 and 13 is defined in terms of a result to be achieved so that it is rendered unclear, i.e. " is capable of converting at least...".

Claims 11 and 13 do not meet the requirements of **Article 6 PCT**.

2. The description at page 10 is not in agreement with new claim 8 since the catalytic partial oxidation process has not been amended to step.

Replaced
by art 34
invention
WO 00/69990

Moreover, in order to operate such process no less than three different hydrocarbon charges have to be used to supply the main conversion processes.

5 It has now been found that flexibility can be improved by further process integration to the extent that part of the product obtained in a hydrocracking operation should be used as feedstock for producing hydrogen which is used in the hydrocracking operation to produce the desired refinery products. The hydrocracking
10 operation should be carried out in such a way that, depending on the product slate envisaged, a fraction is produced which can be used optimally in the production of hydrogen. This means that the process according to the present invention achieves the combined goals of
15 reconstituting the feedstock by the treatment in the hydrocracker whilst at the same time producing or increasing the amount of the fraction which is elected to serve in toto or in part as feedstock for the hydrogen production facility to be used in the hydrocracking
20 operation.

The present invention therefore relates to a method for producing hydrogen and a hydroprocessed product from a hydrocarbonaceous feedstock by subjecting it to a catalytic hydrocracking treatment using hydrogen which
25 has been at least partly produced from hydrocracked feedstock and subjecting at least part of the hydrocracked feedstock, after having subjected it to a separation treatment in the event that hydroprocessed product is to be recovered, to a treatment to produce
30 hydrogen in a single operation which hydrogen is at least partly recovered as product.

The method according to the present invention comprises therefore in essence a hydrocracking operation, optionally a separation operation and a hydrogen

production operation provided with the appropriate feed inlet, product outlet(s) and hydrogen transfer line(s).

The method according to the present invention can be carried out in a number of ways, depending on the nature of the feedstock, the severity of the intended hydro-cracking operation and the type and amount of the specific hydrocracked feedstock fraction to be used as feedstock for the hydrogen producing facility.

Hydrocarbonaceous feedstocks which can be suitably applied in the method according to the present invention are those ranging from having an initial boiling point of about ambient to those having a final boiling point of about 650 °C, measured under standard conditions of temperature and pressure (20 °C and 1 atmosphere). It will be clear that feedstocks which can be applied in the method according to the present invention do not need to have a boiling range profile encompassing the total range disclosed hereinabove. Feedstocks having a boiling point range such that their 90% boiling point (i.e. the temperature at which 90% of the feedstock would have been distilled off in a distillation process) lies in the range between 400 and 600 °C can be advantageously applied. Preference is given to feedstocks having a 90% boiling point in the range between 450 and 600 °C. Good results can be obtained with feedstocks having a 90% boiling point in the range from 475 to 550 °C.

Examples of feedstocks which can be suitably applied are naphtha, kerosene and various types of gas oils such as atmospheric gas oil and vacuum gas oil. Also cycle oils can be suitably applied. Not only feedstocks from mineral origin but also from synthetic origin can be applied. Synthetic or semi-synthetic feedstocks are preferred from a low sulphur and/or nitrogen point of view as such feedstocks reduce the necessity of having sulphur and/or nitrogen removing processes forming part

of product upgrading. Hydrocarbonaceous materials formed from syngas via the so-called Fischer-Tropsch process form a very useful feedstock for the method according to the present invention as such feedstocks would obviate the need for sulphur and/or nitrogen treatment and removal facilities.

It is possible that the hydrocarbonaceous feedstocks to be applied in the method according to the present invention contain also materials boiling below ambient temperature. Such materials may be present in the feedstock to be applied or can be added to such feedstock. Reference is made to the presence of lower hydrocarbons or hydrocarbon fractions such as liquefied petroleum gas.

It is advantageous to use a feedstock which contains between 5 and 40% by weight of material having a boiling point range which is higher than the boiling point range of the hydroprocessed product.

Feedstocks containing sulphur containing materials can also be processed. Normally, the amount of sulphur will not exceed 5% by weight, and preferably will not exceed 3% by weight. Preference is given to feedstocks containing even lower amounts of sulphur, or no sulphur at all.

It will be clear to those skilled in the art that extraneous hydrogen will have to be introduced in the context of the start-up of the method according to the present invention. Part or all of the hydrogen to be consumed during the hydrocracking step of the method according to the present invention will be generated in the hydrogen manufacturing unit forming part of the line-up.

The catalytic hydrocracking treatment in according with the present invention can be suitably carried out at temperatures in the range between 200 and 550 °C,

preferably between 250 and 450 °C. Pressures up to 400 bar can be suitably applied, preference is given to pressures in the range between 10 and 200 atmospheres.

5 In the method according to the present invention at least part of the hydrogen to be used in the hydrocracking treatment will be generated from hydrocracked feedstock. Therefore, catalyst are preferably used which are capable of converting not only that part of the feedstock which delivers the hydroprocessed product but
10 also of converting other parts of the feedstock to such an extent that the remaining hydrocracked feedstock is a good source for hydrogen production. In other words, preference is given to catalysts which also produce large amounts of lower boiling materials (besides the hydrocracked product).
15

Examples of catalysts which can be used in the hydrocracking treatment in accordance with the method in accordance with the present invention are zeolitic catalysts having a tendency to overcrack hydrocarbonaceous material from a conventional point of view (in which as far as possible only those fractions of the feedstock are cracked which deliver the desired hydrocrackate whilst preserving as much as possible of the initial feedstock, or at least to the extent that
20 liquid material will remain and therefore minimising the production of gaseous material). In the method in accordance with the present invention, it is advantageous to apply hydrocracking catalysts which are capable of producing besides the desired product(s) also a fair
25 amount of lower boiling materials, which from a conventional hydrocracking point of view is not preferred at all. Examples of such catalysts can be based on zeolite beta, zeolite Y, ZSM-5, erionite and chabazite. It will be clear to those skilled in the art which
30 specific zeolite material and which specific metal(s)
35

having hydrocracking capabilities can be used, taking into account that preference is given to catalysts giving rather high yields on relatively light products as such products reduce the severity of that part of the process which is directed at the production of hydrogen. As an example suitable catalysts comprise zeolite beta containing one or more of Group VI and/or one or more of Group VIII metals. Examples of Group VI metals comprise Mo and W. Examples of Group VIII metals comprise Ni, Co, Pt and Pd. Suitable catalysts contain between 2 and 40% by weight of Group VI metals and/or between 0.1 and 10% by weight of Group VIII metals. Suitably, the catalysts are supported catalysts. Examples of suitable supports are alumina, silica, silica-alumina, magnesia, zirconia and mixtures of two or more of such supports. Alumina is a preferred support material, optionally in combination with silica-alumina.

Also combinations of two or more catalysts can be suitably applied. Examples of catalyst combinations include so-called stacked-bed catalysts which comprise using different beds filled with (different) catalytic material. The choice of the specific combinations of catalyst beds will be dependent on the process mode envisaged as is known to those skilled in the art.

An important embodiment of the method according to the present invention is one wherein kerosene and/or gas oil is (are) the hydroprocessed product(s) to be recovered from the process whilst hydrogen is produced in an amount exceeding the amount required to satisfy the internal needs of the process.

The remaining hydrocracked feedstock, optionally in combination with part, or even all of the hydroprocessed product in cases when there is no direct outlet for that product, will then be subjected to a treatment to produce hydrogen in a single operation of which at least part is

recovered as product (in addition to the amount used to satisfy the hydrogen requirement (consumption) of the method according to the present invention). The surplus hydrogen can be used as export hydrogen which as such is then available for various applications, such as chemical reagent or as a source for producing electricity.

The process according to the invention allows for the production of hydrogen of good quality, i.e. hydrogen having a purity of at least 80%, preferably at least 90% which enlarges the window of operation.

It will be clear that during start-up procedures, use will have to be made of an outside hydrogen source until the process is at least partly self-sufficient with respect to its hydrogen consumption. For instance, use can be made of hydrogen available in storage containers.

As some hydrogen may already be present in the feedstock to the hydrogen-producing machine, it can be useful to separate it and use it as part of the amount of hydrogen needed to satisfy the hydrogen requirement of the process. This can be conveniently done by subjecting the hydrocracked feedstock to a separation process involving a membrane which will allow passage of hydrogen whilst retaining heavier molecules. Those skilled in the art know which membrane to use and how to operate such membrane.

There are many processes known in the art which are capable of producing hydrogen from hydrocarbonaceous feedstocks. Those skilled in the art know such processes and how to operate them. Producing hydrogen in a single operation can be carried out in one vessel but optionally in two or more vessels such as in a unit which is composed of a catalytic partial oxidation step and one or more shift conversion steps. A convenient process is catalytic (partial) oxidation. Other suitable processes

are steam-methane reforming and catalytic dehydrogenation of lower alkanes such as propane or butane.

A preferred hydrogen-producing system can be found in the combination of catalytic partial oxidation and the
5 watergas-shift reaction which last reaction, in essence, converts carbon monoxide, produced together with hydrogen in the catalytic partial oxidation reaction, in the presence of water (steam under the process conditions) to hydrogen and carbon dioxide. The net result of the
10 combined catalytic oxidation/watergas-shift reaction is that hydrocarbonaceous material is converted into hydrogen and carbon dioxide.

Normally, the combined catalytic partial oxidation/
watergas-shift process can be operated at a efficiency of
15 at least 50%, calculated on hydrogen produced, preferably with an efficiency of at least 65%, calculated on hydrogen produced (not taking into account hydrogen present in the hydrocracked feedstock).

Suitable catalysts for the catalytic partial
20 oxidation process in accordance with the method according to the present invention comprise one or more metals of Group VIII of the Periodic Table of the Elements supported on a carrier. Examples of suitable metals comprise rhodium, iridium and ruthenium as well as
25 combination of two or more of these metals. Especially carriers having a high tortuosity can be suitably applied. Suitable process conditions comprise using oxygen:carbon molar ratios in the range between 0.30 and 0.80, preferably between 0.45 and 0.75, and most
30 preferably between 0.45 and 0.65; temperatures between 800 °C and 1200 °C, in particular between 900 °C and 1100 °C whilst using a gas velocity in the range between 100,000 and 10,000,000 l/kg/hr, preferably in the range between 250,000 and 2,000,000 l/kg/hr.

An advantage of the method according to the present invention is that when hydrogen is produced as the main product, carbon dioxide is produced at the same time in appreciable amounts which may be useful for commercial operations such as for enhanced oil recovery or for heating purposes in the event that an appropriate infrastructure is available (such as urban communities and/or green-house agriculture).

Since feedstocks containing up to about 5 %wt of sulphur can be used in the method according to the present invention, the treatment with hydrogen will cause production of hydrogen sulphide. It will be clear that in such instances a further process step will be necessary to remove hydrogen sulphide from the hydrocracked feedstock and to convert it into sulphur. When the pressure is released prior to separating off the hydroprocessed product, hydrogen sulphide will be removed preferentially and can be sent to a further processing unit such as a SCOT-unit, or, if the concentration of hydrogen is large enough it can be fed directly to a CLAUS-unit. Those skilled in the art know such processing facilities and how to operate them.

Various embodiments of the method according to the present invention can be schematically illustrated by means of Figure 1.

In Figure 1 an embodiment is illustrated in which a sulphur-containing feedstock is processed in such a way as to deliver at least one hydroprocessed product to be recovered as marketable product together with hydrogen produced for use in the process according to the present invention as well as for export.

A feedstock is introduced via line 1 into hydrocracking unit 10 in which the feedstock is subjected to a catalytic treatment with hydrogen under hydrocracking conditions. Hydrogen is introduced into line 1 via

cracked feedstock via line 4 to hydrogen sulphide removal unit 30 whereafter the further steps are as depicted in Figure 1.

5 A further embodiment in accordance with the method according to the invention is that wherein use is made of a sulphur-free feedstock (i.e. of a feedstock of synthetic or semi-synthetic nature or of a feedstock which has already been subjected to a hydrodesulphurisation treatment). In such embodiment, it is not
10 longer necessary to separate off a hydrogen sulphide containing hydrocracked feedstock (or to send the total hydrocracked feedstock to the (optional) hydrogen separating unit) which means that the process as schematically represented in Figure 1 is now operated
15 without using hydrogen sulphide removal unit 30.

Examples

The method according to the present invention can be illustrated by the following prophetic examples.

Example 1

20 A hydrocarbonaceous feedstock having an IBP of 121 °C and a 90% boiling point of 533 °C and containing 0.02% by weight of sulphur can be passed (in an amount of 10 tons/day together with 1.5 tons/day of hydrogen, representative for the hydrogen/feedstock ratio) over a
25 zeolite beta type alumina supported catalyst in hydrocracking unit 10 under conditions to convert in single pass 90 %wt of the feedstock to lower boiling material. As product, 45 %wt, calculated on hydrocarbonaceous feedstock intake, of a hydroprocessed
30 product (comprising kerosene and gas oil) can be obtained whilst the remaining hydrocracked feedstock can be sent to the hydrogen sulphide removal unit. After separating off hydrogen present in the hydrocracked feedstock (and returning it to the feedstock to be used as part of the
35 hydrogen needed in the hydrocracking unit) after leaving

C L A I M S

1. Method for producing hydrogen and a hydroprocessed product from a hydrocarbonaceous feedstock, by subjecting it to a catalytic hydrocracking treatment using hydrogen which has been at least partly produced from hydrocracked feedstock and subjecting at least part of the hydrocracked feedstock, after having subjected it to a separation treatment in the event that hydroprocessed product is to be recovered, to a treatment to produce hydrogen in a single operation which hydrogen is at least partly recovered as product.

2. Method according to claim 1, in which use is made of feedstocks ranging from those having an initial boiling point of about ambient to those having a final boiling point of about 650 °C.

3. Method according to claim 2, in which use is made of feedstocks having a boiling point range such that their 90% boiling point lies in the range between 400 °C and 600 °C.

4. Method according to one or more of claims 1-3, in which use is made of feedstocks having a sulphur content of not more than 5 %wt, preferably below 3 %wt.

5. Method according to one or more of claims 1-4, in which a hydrocarbonaceous feedstock is used containing between 5 and 40 %wt of material having a boiling point range which is the same or higher than the boiling point range of the hydrocracked product to be recovered.

6. Method according to one or more of claims 1-5, in which kerosene and/or gas oil are recovered as hydrocracked products from the hydrocracked feedstock.

7. Method according to one or more of claims 1-6, in which part or all of the non-recovered material from the

treatment with hydrogen is subjected to a catalytic oxidation process which produces hydrogen and carbon (di)oxide.

8. Method according to claim 7, in which the catalytic oxidation process comprises a catalytic partial oxidation process and a watergas-shift process.

9. Method according to one or more of claims 1-8, in which kerosene and/or gas oil and hydrogen are produced from no feedstocks other than the hydrocarbonaceous feedstock and water used in the watergas-shift step.

10. Method according to one or more of claims 1-9, in which hydrogen sulphide generated by the hydrocracking treatment is converted into elemental sulphur by conventional means.

11. Method according to one or more of claims 1-10, in which use is made of a catalyst system capable of converting at least 50 %wt, preferably at least 65 %wt of the material having a boiling point range which is higher than the boiling point range of the hydroprocessed product.

12. Method according to claim 11, in which use is made of a hydrocracking catalyst containing zeolite beta as active component.

13. Method according to claim 12, in which the zeolite beta-based catalyst is capable of converting at least 90 %wt of the fraction to be treated to obtain the hydroprocessed product.

14. Method according to one or more of claims 11-13, in which the hydrocracking treatment is carried out at a temperature between 200 and 550 °C, preferably at a temperature between 250 and 450 °C.

15. Method according to one or more of claims 11-14, in which the hydrocracking treatment is carried out at a pressure up to 400 atmospheres, preferably at a pressure between 10 and 200 atmospheres.

16. Method according to one or more of claims 7-15, in which the hydrogen generated by the catalytic oxidation step has been produced at least partly from hydrocarbons containing at most 4 carbon atoms present in the hydrocarbonaceous feedstock or as produced during the hydrocracking treatment.

17. Method according to claim 16, in which the feedstock to the catalytic oxidation step consists of hydrocarbons having 4 or less carbon atoms.

18. Method according to one or more of claims 1-17, in which hydrogen is separated off from the hydrocracked feedstock and from the hydroprocessed product if the latter is not to be recovered prior to the hydrogen manufacturing step.